

DESCRIPTION

LUBRICANT FOR WATER-BASED METAL WORKING OIL

5 TECHNICAL FIELD

The present invention relates to a lubricant for water-based metal working oil, and detailedly to polyether lubricant for water-based metal working oil, lubricant composition for water-based metal working oil and water-based metal working oil.

BACKGROUND ART

Examples of water-based metal working oils such as cutting oil, rolling oil, drawing oil, pressing oil, forging oil, abrasive working oil for aluminum disk, abrasive oil for silicon wafer and coolant for cutting silicon wafer include solution type, soluble type and emulsion type.

Performances required therefor are lubricity, low-foaming property, water dilution stability (stability of a diluent diluted with water during use) and oil separation property from other mineral oil-based working oil.

Polyether has been conventionally used as a lubricant used for water-based metal working oil. The polyether is, so-called Pluronic type or counter Pluronic type, a block copolymer of ethylene oxide and propylene oxide (for example, refer to U. S. Patents No. 4,414,121 and 4,636,321) or a random copolymer of ethylene oxide and propylene oxide.

Polyethylene oxide chain contained in the polyether is introduced in order to improve water dilution stability by increasing hydrophilicity, and the polyether generally has an average molecular weight of 800 or more in order to improve lubricity.

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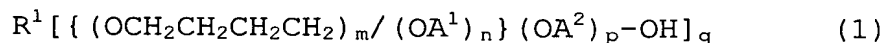
SUMMARY OF THE INVENTION

The object of the present invention is to provide a lubricant for water-based metal working oil, which is superior in lubricity to steel materials as well as,
 5 particularly, lubricity to soft metal such as aluminum.

Another object of the present invention is to provide a lubricant composition for water-based metal working oil, which comprises the above-mentioned lubricant and other additives and is superior in lubricity.

10 A further object of the present invention is to provide water-based metal working oil which comprises water and the above-mentioned lubricant or the above-mentioned lubricant composition, and is superior in lubricity, low-foaming property, water dilution stability and oil
 15 separation property.

According to the present invention, the above-mentioned object is completed by a lubricant for water-based metal working oil (hereinafter abbreviated as a lubricant) containing polyether (E) represented by the
 20 following general formula (1) and having an HLB of 6.1 to 16.0 and a weight-average molecular weight of 500 to 10,000.



In the formula, R^1 denotes a residue such that at least one hydroxyl group is removed from a compound with a carbon number of 1 to 24 having 1 to 6 hydroxyl group(s);
 25 A^1 denotes an alkylene group with a carbon number of 2 to 4 except a 1,4-butylene group; A^2 denotes an alkylene group with a carbon number of 2 to 4; m denotes an integer of 1 or more having an average of 1 to 120; n and p each denotes an integer of 0, 1 or more such that the average of $(n+p)$
 30 is 1 to 200, and n and p are not simultaneously 0; q denotes an integer of 1 to 6; and $\{(OCH_2CH_2CH_2CH_2)_m/(OA^1)_n\}$ in the case where n is an integer of 1 or more denotes a random bond.

35 The present invention is also a lubricant composition

for water-based metal working oil, which comprises the above-mentioned polyether (E) and other additives.

The present invention is also water-based metal working oil which comprises water and the above-mentioned lubricant or the above-mentioned lubricant composition, and contains the polyether (E) of 0.01 to 95 weight % in quantity on the basis of the weight of the above-mentioned metal working oil.

10 DETAILED DESCRIPTION OF THE INVENTION

In the general formula (1) of the present invention, R^1 is a residue such that at least one hydroxyl group, preferably all hydroxyl groups, is removed from a compound with a carbon number of 1 to 24 having 1 to 6 hydroxyl group(s).

Examples of R^1 include a residue of linear, branched or alicyclic monohydric to hexahydric aliphatic alcohols, a residue of monohydric to hexahydric phenols, a residue of monohydric to hexahydric aromatic group-containing aliphatic alcohols, a residue of heterocyclic dihydric alcohols, and a residue of sugars and derivatives thereof.

Examples of these alcohols and phenols include the following (e1) to (e5).

- (e1) aliphatic alcohols
- 25 (e11) monohydric alcohols
 - (e111) linear or branched aliphatic saturated monohydric alcohols with a carbon number of 1 to 24:
 - methanol, ethanol, propanol (such as n-propanol and isopropanol), butanol, pentanol, hexanol, heptanol, octanol
 - 30 (such as n-octanol and 2-ethylhexyl alcohol), nonyl alcohol, decyl alcohol, undecyl alcohol, dodecyl alcohol, tridecyl alcohol (such as n-tridecyl alcohol and isotridecyl alcohol), tetradecyl alcohol, pentadecyl alcohol, hexadecyl alcohol, heptadecyl alcohol, octadecyl alcohol, nonadecyl
 - 35 alcohol, eicosyl alcohol, heneicosyl alcohol, docosyl

- alcohol, tricosyl alcohol, tetracosyl alcohol, and the like
 (e112) linear or branched aliphatic unsaturated monohydric
 alcohols with a carbon number of 3 to 24:
 alkenyl alcohol (such as 1-, 2- or iso-propenyl alcohol,
 5 butenyl alcohol, pentenyl alcohol, hexenyl alcohol,
 heptenyl alcohol, octenyl alcohol, nonenyl alcohol, decenyl
 alcohol, undecenyl alcohol, dodecenyl alcohol, tridecenyl
 alcohol, tetradecenyl alcohol, pentadecenyl alcohol,
 hexadecenyl alcohol, heptadecenyl alcohol, octadecenyl
 10 alcohol, nonadecenyl alcohol, eicosenyl alcohol,
 heneicosenyl alcohol, docosenyl alcohol, tricosenyl alcohol
 and tetracosenyl alcohol), and alkynyl alcohol (such as
 pentynyl alcohol)
 (e113) alicyclic monohydric alcohols with a carbon number
 15 of 4 to 24:
 cyclopentanol, cyclohexanol, and the like
 (e12) dihydric alcohols
 (e121) linear or branched aliphatic dihydric alcohols with
 a carbon number of 2 to 24:
 20 alkylene glycol (such as ethylene glycol, propylene glycol,
 1,3-, 1,4- or 1,2-butanediol, neopentyl glycol, 1,6-
 hexanediol, 1,2- or 1,7-heptanediol, 1,2- or 1,8-octanediol,
 isobutylene glycol, 3-methyl-1,5-pentanediol, 2,2,4-
 trimethyl-1,3-pentanediol, 2,2-dimethyl-1,3-propanediol, 2-
 25 butyl-2-ethyl-1,3-propanediol and 2,5-dimethylhexane-2,5-
 diol)
 (e122) alicyclic dihydric alcohols with a carbon number of
 4 to 18:
 cycloalkylene glycol (such as 1,4-cyclohexanediol and 1,4-
 30 cyclohexanedimethanol), hydrogenated bisphenols (such as
 hydrogenated bisphenol A and hydrogenated bisphenol F), and
 the like
 (e13) trihydric to hexahydric alcohols
 (e131) linear or branched trihydric aliphatic alcohols with
 35 a carbon number of 3 to 24:

- glycerin, 1,2,3-butanetriol, 1,2,3-pentanetriol, 2-methyl-1,2,3-propanetriol, 2-methyl-2,3,4-butanetriol, 2-ethyl-1,2,3-butanetriol, 2,3,4-pentanetriol, 2,3,4-hexanetriol, 4-propyl-3,4,5-heptanetriol, 2,4-dimethyl-2,3,4-
- 5 pentanetriol, pentamethylglycerin, 1,2,4-butanetriol, 1,2,4-pentanetriol, trimethylolethane, trimethylolpropane, and the like
- (e132) linear or branched tetrahydric to hexahydric aliphatic alcohols with a carbon number of 5 to 24 and
- 10 intramolecular or intermolecular dehydrate thereof: pentaerythritol, dipentaerythritol, sorbitol, mannitol, 1,5-, 3,6- or 1,4-sorbitan, diglycerol
- (e2) phenols
- (e21) monohydric phenols with a carbon number of 6 to 24:
- 15 phenol, alkylphenol (such as o-, m-, or p-methyl phenol, 2,3-, 2,4-, 2,5-, 3,4- or 3,5-dimethylphenol, 2,6-dimethylphenol, o-, m-, or p-ethyl phenol, p-n-butylphenol, p-octyl phenol and p-nonyl phenol), monostyrylphenol, monobenzylphenol, and the like
- 20 (e22) dihydric to hexahydric phenols with a carbon number of 6 to 24:
- dihydric phenol (such as catechol, resorcin and hydroquinone), trihydric to hexahydric phenol (such as trioxybenzene, tetraoxybenzene and hexaoxybenzene),
- 25 bisphenols (such as bisphenol A and bisphenol F), and the like
- (e3) aromatic group-containing aliphatic alcohols
- (e31) aralkyl alcohols with a carbon number of 7 to 24: benzyl alcohol, phenethyl alcohol, and the like
- 30 (e32) substituted aralkyl alcohols with a carbon number of 8 to 24:
- o-, m-, or p-methyl benzyl alcohol, p-n-butyl phenethyl alcohol, and the like
- (e4) heterocyclic dihydric alcohols:
- 35 1,4,3,6-sorbide, and the like

(e5) sugars and derivatives thereof:

sucrose, glucose, mannose, fructose, methyl glucoside, and the like

Among these, (e1) is preferable, more preferably
5 (e12) and (e13), particularly preferably (e12) with a carbon number of 2 to 20 and (e13) with a carbon number of 3 to 18, preferably above all (e121), (e131) and (e132) with a carbon number of 3 to 6.

Additionally, R^1 is preferably a residue such that
10 all hydroxyl groups are removed from dihydric or trihydric alcohol.

R^1 with a carbon number of more than 24 renders the hydrophilicity of (E) insufficient, and thereby renders poor the water dilution stability of the after-mentioned
15 water-based metal working oil employing (E) as a lubricant, so that separation is occasionally caused after dilution.

A^1 in the general formula (1) is an alkylene group with a carbon number of 2 to 4 except a 1,4-butylene group, and A^2 is an alkylene group with a carbon number of 2 to 4.
20 A^1 and A^2 may be identical or different. Examples of A^1 include an ethylene group, a 1,2- or 1,3-propylene group, a 1,2- or 2,3-butylene group and an isobutylene group, and in the case of plural A^1 , two kinds or more thereof may be used together. Examples of A^2 include a 1,4-butylene group
25 in addition to the examples of A^1 , and in the case of plural A^2 , two kinds or more may be used together.

A^1 and A^2 each is preferably an ethylene group, a 1,2-propylene group and a 1,2-butylene group, more preferably an ethylene group and a 1,2-propylene group,
30 particularly preferably an ethylene group from the viewpoint of improving water dilution stability. The presence of an ethylene group in at least a part of A^1 or A^2 improves water solubility of (E). In the general formula (1), a compound in which A^2 is an ethylene group is
35 preferable.

m, n, p and q in the general formula (1) each is selected from the following range so that the weight-average molecular weight (hereinafter abbreviated as Mw) of (E) is 500 to 10,000.

5 (E) in the present invention generally has molecular-weight distribution, whereby m, n, p and q in the general formula (1) have a multitude of combinations in the following range and (E) may be a mixture thereof or one kind thereof.

10 m is an integer of 1 or more, preferably 1 to 120, more preferably 1 to 30, having an average of 1 to 120, preferably 1 to 30, more preferably 1 to 14.

n and p each is an integer of 0, 1 or more, preferably 0 or 1 to 200, more preferably 0 or 1 to 40,

15 such that the average of (n+p) is 1 to 200, preferably 2 to 57, more preferably 2 to 16.

p is 1 to 200 in the case where n is 0, while n is 1 to 200 in the case where p is 0, and n and p are not simultaneously 0.

20 n preferably has an average of 0 to 14, more preferably 2 to 14. p preferably has an average of 0 to 44, more preferably 0 to 12, particularly preferably 0. In the general formula (1), it is preferable that n or p is 0.

25 m/n is preferably 0.1 to 4, more preferably 0.2 to 3 from the viewpoint of water dilution stability.

p/(m+n) is preferably 0 to 3, more preferably 0 to 0.2 from the viewpoint of water dilution stability.

m/(m+n+p) is preferably 0.05 to 0.8, more preferably 0.1 to 0.7 from the viewpoint of water dilution stability.

30 q is an integer of 1 to 6, preferably 2 to 6, more preferably 2 to 4, particularly preferably 2 to 3 from the viewpoint that water dilution stability is excellent. q of more than 6 renders lubricity poor.

35 Mw (measured by gel permeation chromatography) of (E) is 500 to 10,000, preferably 700 to 7,000, more preferably

800 to 6,000, particularly preferably 1,000 to 5,000. Mw of less than 500 in (E) renders lubricity insufficient, while Mw of more than 10,000 renders kinematic viscosity too higher and thereby renders poor the handling property in compounding and the like.

With regard to polyether (E), $(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$ and (OA^1) in the formula (1) need to be random bonds; otherwise the flowability of (E) at low temperature is rendered insufficient and the handling property of a lubricant is rendered poor.

HLB of (E) is 6.1 to 16.0, preferably 6.3 to 13.8, more preferably 8 to 13. An HLB of less than 6.1 renders the hydrophilicity of (E) insufficient, and thereby renders water dilution stability poor, so that separation is occasionally caused after dilution. An HLB of more than 16.0 renders lubricity poor.

HLB in the present invention is HLB by Oda method, which can be calculated from the ratio of a value of organic property to a value of inorganic property in a compound by a method of calculation described on page 197 of 'New Introduction to Surface Active Agents' (1996, published by Sanyo Chemical Industries, Ltd.).

The cloud point of (E) is preferably high from the viewpoint of water dilution stability, preferably 5 to 60°C in consideration of the viewpoint of lubricity. The cloud point in the present invention is a temperature at which a 2-weight % aqueous solution of (E) is heated and then clouding is confirmed by visual observation.

(E) is generally in a liquid state at normal temperature and kinematic viscosity thereof is preferably 5 to 1,000 mm^2/s at 40°C. The kinematic viscosity can be measured in accordance with JIS K 2283 (the kinematic viscosity is hereinafter measured in the same manner).

(E) can be manufactured by the following processes:
(i) a process such that tetrahydrofuran (hereinafter

abbreviated as THF) and one kind or more of alkylene oxide (hereinafter abbreviated as AO) with a carbon number of 2 to 4 except THF are subject to a random addition reaction to the above-mentioned (e1) to (e5) in the presence of a catalyst, and thereafter one kind or more of AO with a carbon number of 2 to 4 is further added thereto as required; and

(ii) in the case of polyether in which n in the general formula (1) is 0, a process such that only THF is subjected to homopolymerization with (e1) to (e5) in the presence of a catalyst for synthesizing polyoxytetramethylene glycol (hereinafter abbreviated as PTMG), and one kind or more of AO with a carbon number of 2 to 4 is further added thereto in the presence of a catalyst.

The temperature of addition reactions in (i) and (ii) is preferably 30 to 120°C, and the pressure thereof is preferably 0 to 0.6 MPa.

Examples of AO used for addition reactions include ethylene oxide (EO), propylene oxide (PO), 1,2-butylene oxide, 2,3-butylene oxide and isobutylene oxide.

A conventionally known catalyst can be used as the catalyst, and the kind of preferable catalyst differs between a THF/AO random addition reaction and an AO addition reaction.

Examples of the catalyst for a THF/AO random addition reaction include the following:

Lewis acid and a complex thereof; BF_3 , BCl_3 , AlCl_3 , FeCl_3 , SnCl_3 , BF_3 •ether complex, BF_3 •THF complex (hereinafter abbreviated as BF_3 •THF), and the like

proton acid; H_2SO_4 , HClO_4 , and the like
perchlorate of alkali metal; KClO_4 , NaClO_4 , and the like

perchlorate of alkaline earth metal; $\text{Ca}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2$, and the like

perchlorate of metal except the above; $\text{Al}(\text{ClO}_4)_3$, and

the like

Among these, $\text{BF}_3 \cdot \text{ether}$ complex and $\text{BF}_3 \cdot \text{THF}$ are preferable.

5 Examples of the catalyst for an AO addition reaction include the following in addition to the above-mentioned catalyst:

hydroxide of alkali metal or alkaline earth metal; KOH, NaOH, CsOH, $\text{Ca}(\text{OH})_2$, and the like

10 oxide of alkali metal or alkaline earth metal; K_2O , CaO, BaO, and the like

alkali metal and a hydride thereof; Na, K, NaH, KH, and the like

amines; triethylamine, trimethylamine, and the like

15 Among these, KOH, NaOH, CsOH, $\text{BF}_3 \cdot \text{ether}$ complex and $\text{BF}_3 \cdot \text{THF}$ are preferable.

A lubricant composition for water-based metal working oil (hereinafter abbreviated as a lubricant composition) of the present invention comprises the above-mentioned (E) and other additives.

20 Examples of other additives include one kind or more selected from the group consisting of aliphatic carboxylic acid with a carbon number of 8 to 22 and/or a salt thereof (F), other polyether (G), an antioxidant (H), an extreme-pressure additive (I), a rust preventive (J) and an
25 antifoaming agent (K).

Examples of (F) include the following compounds (F1) to (F3).

(F1) aliphatic monocarboxylic acids

(F11) saturated aliphatic monocarboxylic acids:

30 octylic acid (such as caprylic acid and isooctylic acid), nonanoic acid, decanoic acid (such as capric acid), undecanoic acid, dodecanoic acid (such as lauric acid) and the like, preferably octylic acid, nonanoic acid and decanoic acid, more preferably caprylic acid and nonanoic
35 acid

(F12) unsaturated aliphatic monocarboxylic acids:

lindelic acid, sperm acid, myristoleic acid, palmitoleic acid, oleic acid, erucic acid and the like, preferably oleic acid

5 (F2) aliphatic dicarboxylic acids:

α,ω -dicarboxylic acid (such as azelaic acid, sebacic acid and dodecanedioic acid) and alkenyl succinic acid (such as octenyl succinic acid, dodecenyl succinic acid and pentadecenyl succinic acid), preferably alkenyl succinic
10 acid, particularly preferably dodecenyl succinic acid and pentadecenyl succinic acid

(F3) a salt of the above-mentioned monocarboxylic acid or dicarboxylic acid

Examples of the salt include alkali metallic salt,
15 alkaline earth metallic salt, ammonium salt, aliphatic amine salt and salt of AO adduct of aliphatic amine.

Examples of the salt include neutralized product of (F1) or (F2) by a neutralizer.

Examples of the neutralizer include hydroxide of
20 alkali metal (such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide); hydroxide of alkaline earth metal (such as calcium hydroxide and magnesium hydroxide); ammonia; aliphatic amine [alkylamine or alkenylamine with a carbon number of 1 to 10 or more
25 (such as laurylamine and oleylamine), heterocyclic amine with a carbon number of 3 to 10 (such as morpholine) and mono-, di- or trialkanolamine with a carbon number of 2 to 10 in an alkanol group (such as monoethanolamine, triethanolamine, isopropanolamine and N-
30 dimethylaminoethanolamine)]; and AO adduct of these amines. Two kinds or more thereof may be used together.

Examples of the above-mentioned AO adduct of the amines include AO adduct of alkylmonoamine with a carbon number of 1 to 10 or more in an alkyl group (such as
35 methylamine, ethylamine, diethylamine, propylamine,

butylamine, cyclohexylamine and octylamine); AO adduct of alkylenediamine with a carbon number of 2 to 18 or more in an alkylene group (such as ethylenediamine, propylenediamine, hexylenediamine, octylenediamine, 5 decylenediamine and dodecylenediamine); and AO adduct of polyalkylene polyamine with a total carbon number of 4 to 18 or more, a carbon number of 2 to 6 in an alkylene group and preferably 3 to 7 amines (such as polyethylene polyamines, for example, diethylenetriamine, 10 triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and hexaethyleneheptamine). Examples of AO include ones with a carbon number of 2 to 4 such as EO and PO (preferably PO), and the added number of moles of AO is preferably 0.5 to 2 mol with respect to one N atom of 15 an amine, more preferably 1 to 2 mol. The added number of 0.5 to 2 mol renders excellent the oil separation property of water-based metal working oil.

Among the neutralizers, aliphatic amine and AO adduct thereof are preferable, more preferably AO adduct, 20 particularly preferably 2 to 8 mol of PO adduct of triethanolamine and ethylenediamine, particularly, 4 mol of PO adduct of triethanolamine and ethylenediamine, and 3 to 8 mol of PO adduct of diethylenetriamine, particularly, 5 mol of PO adduct of diethylenetriamine.

25 Examples of a dicarboxylic acid salt also include mono salts of dicarboxylic acid.

A lubricant composition of the present invention is preferable in that containing (F) therein restrains foaming of metal working oil during dilution by water.

30 A carbon number of 8 or more in (F) less causes a lubricant composition to easily rust metal, while a carbon number of 22 or less therein causes less foaming even during dilution by water.

With regard to a weight ratio in the case of using 35 together monocarboxylic acid (salt) [carboxylic acid (salt)

hereinafter denotes carboxylic acid and/or a salt thereof] and dicarboxylic acid (salt), the ratio of monocarboxylic acid (salt) to dicarboxylic acid (salt) is preferably (100 to 5):(0 to 95) from the viewpoint of lubricity, more
5 preferably (100 to 10):(0 to 90).

The equivalent ratio of carboxylic acid to carboxylic acid salt in a mixture of carboxylic acid and carboxylic acid salt is preferably (0 to 50):(50 to 100), more preferably (0 to 30):(70 to 100).

10 In the case of using carboxylic acid salt, carboxylic acid salt may be directly added, or carboxylic acid and a neutralizer may be so separately added as to form carboxylic acid salt by neutralizing in a compounding step. A process of neutralizing in a compounding step is
15 preferable.

In the case of using aliphatic amine or AO adduct thereof as a neutralizer, the equivalent ratio of carboxylic acid to a neutralizer is preferably 1:0.8 to 1:3, more preferably 1:0.9 to 1:2, and excessive carboxylic acid
20 in the case where carboxylic acid is excessive functions generally as not merely restraint of foaming but also an oiliness agent component.

On the contrary, excessive aliphatic amine or AO adduct thereof in the case where a neutralizer is excessive
25 functions as a rust preventive component in a lubricant composition and is not included in the content of (F) but in the content of the after-mentioned rust preventive (J).

In the case where a small quantity of generated water by neutralization [preferably less than 5% on the basis of
30 the weight of (E)] is generated in a process of neutralizing in a compounding step, the water is also included in a component of a lubricant composition of the present invention.

The content ratio of (F) to (E) is generally 0.03 to
35 10 at a weight ratio, preferably 0.03 to 5.0, more

preferably 0.06 to 1.2, particularly preferably 0.1 to 1.0.

When the ratio of (F) is 0.03 or more, worked metal is hardly rusted and lubricity is easily rendered excellent. When the ratio is 5 or less, the oil separation property of
5 water-based metal working oil is rendered excellent.

Sulfur and/or nitrogen atom-containing carboxylic acid (salt) used as the after-mentioned extreme-pressure additive is not included in (F) of the present invention.

Other polyether (G) is polyether except (E) of the
10 present invention and examples thereof include polyether conventionally used as a lubricant, which has Mw of 500 to 30,000.

Examples of (G) include nonionic polyether (G1) and ionic polyether (G2).

15 Examples of (G1) include polyethylene glycol, EO adduct of monohydric to tetrahydric alcohol with a carbon number of 1 to 24, EO/PO random or block adduct of monohydric to tetrahydric alcohol with a carbon number of 1 to 24, EO/PO/EO block copolymer (so-called 'Pluronic'
20 described in U. S. Patents No. 4,414,121 and 4,636,321), PO/EO/PO block copolymer (so-called 'counter Pluronic'), and terminal-alkoxylated product or terminal-acylated product of the polyether or (E).

Examples of (G2) include anionized products of the
25 above-mentioned (G1) such as sulfate of polyoxyalkylene compound (described in U. S. Patent No. 3,950,258), phosphate thereof (described in U. S. Patent No. 3,945,930) and carboxy-etherified product thereof.

The added quantity of (G) is preferably 90% or less
30 on the basis of the weight of (E) in a lubricant composition (% hereinafter denotes weight % unless otherwise specified), more preferably 60% or less, particularly preferably 30% or less.

Examples of an antioxidant (H) include phenolic
35 antioxidant [such as 2,4-dimethyl-6-tert-butylphenol and

4,4-butyldienebis(6-tert-butylmetacresol)]; aromatic amine antioxidant (such as phenyl- α -naphthylamine and phenyl- β -naphthylamine); zinc dialkyl (a carbon number of 1 to 36) dithiophosphate; zinc diallyl (a carbon number of 2 to 36) dithiophosphate; organic sulfide; and organic selenide.

The added quantity of an antioxidant (H) is preferably 2% or less on the basis of the weight of polyether (E) in a lubricant composition, more preferably 0.0001 to 1%.

Examples of an extreme-pressure additive (I) include lead soap (such as lead naphthenate); sulfur compound (such as sulfurized fatty acid, for example, sulfurized oleic acid, sulfurized fatty acid ester, sulfurized sperm oil, sulfurized terpene, dibenzyl disulfide, amine salt or alkali metal salt of alkyl thio-propionic acid with a carbon number of 8 to 24 and amine salt or alkali metal salt of alkyl thioglycolic acid with a carbon number of 8 to 24); chlorine compound (such as chlorinated stearic acid, chlorinated paraffin and chloronaphthazantate); and phosphorus compound (such as tricresyl phosphate, tributyl phosphate, tricresyl phosphite, n-butyl-di-n-octyl phosphinate, di-n-butyl-dihexyl phosphonate, di-n-butylphenyl phosphonate, dibutyl phosphoroamidate and amine dibutyl phosphate). The added quantity of an extreme-pressure additive (I) is preferably 10% or less on the basis of the weight of polyether (E) in a lubricant composition, more preferably 5% or less.

Examples of a rust preventive (J) include aliphatic carboxylic acid amide with a carbon number of 14 to 36 (such as myristic acid amide, palmitic acid amide and oleylamide); alkenyl succinamide with a carbon number of 6 to 36 (such as octenyl succinamide, dodecenyl succinamide, pentadecenyl succinamide and octenyl succinamide); cyclohexylamine nitrite; benzotriazole; mercaptobenzothiazole; N,N'-disalicylidene-1,2-diaminopropane; alizarin; and aliphatic amine and AO adduct

thereof described as the above-mentioned neutralizer.

Among (J), AO adduct of aliphatic amine is preferable, particularly preferably 2 to 8 mol of PO adduct of triethanolamine and ethylenediamine, particularly, 4 mol of
5 PO adduct of triethanolamine and ethylenediamine, and 3 to 8 mol of PO adduct of diethylenetriamine, particularly, 5 mol of PO adduct of diethylenetriamine.

Aliphatic carboxylic acid amide with a carbon number of 14 to 36 and alkenyl succinamide with a carbon number of
10 6 to 36 function also as an oiliness improver.

The added quantity of a rust preventive (J) is preferably 50% or less on the basis of the weight of polyether (E) in a lubricant composition, more preferably 1 to 40%, and the above-mentioned excessive aliphatic amine
15 is also included in the quantity of (J).

Examples of an antifoaming agent (K) include polyorganosiloxane (such as polydimethylsiloxane). The added quantity of an antifoaming agent (K) is preferably 1,000 ppm or less on the basis of the weight of polyether
20 (E) in a lubricant composition, more preferably 10 to 500 ppm.

A lubricant composition of the present invention preferably contains aliphatic carboxylic acid with a carbon number of 8 to 22 and/or a salt thereof (F) as other
25 additives. A lubricant composition of the present invention also preferably contains as other additives one kind or more selected from the group consisting of an antioxidant, an extreme-pressure additive, a rust preventive and an antifoaming agent.

30 A lubricant composition of the present invention preferably does not contain hydrocarbon oil (such as mineral oil, and animal and vegetable oil). The reason therefor is that no content of hydrocarbon oil renders less the deterioration due to rotting even during preservation
35 for a long period as water-based metal working oil after

adding water.

The percentage (%) of (E)/(F)/(G) to (K) on the basis of the weight of a lubricant composition of the present invention is generally (10 to 99)/(1 to 90)/(0 to 50),
 5 preferably (50 to 90)/(9 to 80)/(1 to 30), more preferably (60 to 90)/(9 to 30)/(1 to 10).

Water-based metal working oil of the present invention contains water and the above-mentioned lubricant or lubricant composition, and contains polyether (E) of
 10 generally 0.01 to 95% in concentration on the basis of the weight of the water-based metal working oil, preferably 0.2 to 90%, more preferably 10 to 85%, particularly preferably 30 to 60%.

Water-based metal working oil of the present
 15 invention contains the lubricant composition of generally 0.01 to 99% in concentration on the basis of the weight of the water-based metal working oil, preferably 0.3 to 95%, more preferably 12 to 88%, particularly preferably 30 to 80%.

20 The concentration of (E) in the water-based metal working oil is preferably 5 to 90%, more preferably 10 to 60% in the case where the water-based metal working oil is conveyed or stored, or used as drawing oil, pressing oil, rolling oil, forging oil and the like.

25 In the case of being used as cutting oil, grinding oil, abrasive working oil for aluminum disk, abrasive oil for silicon wafer and coolant for cutting silicon wafer, the water-based metal working oil particularly preferably contains not merely (E) but also (F) and is preferably
 30 diluted with water immediately before use so that the weight concentration of (E) is 0.5 to 3%, particularly 1 to 2% and the concentration of (F) is 0.1 to 2%, particularly 0.2 to 2%.

Water-based metal working oil of the present
 35 invention can be manufactured by compounding the above-

mentioned lubricant or lubricant composition directly with water, and otherwise each component of the lubricant composition may be separately compounded with water, in which case the order of compounding is not particularly limited.

Water-based metal working oil of the present invention may be subject to any form of solution type, soluble type and emulsion type, preferably solution type or soluble type from the viewpoint of appearance stability of the water-based metal working oil with the passage of day.

In the case of using solution type or soluble type metal working oil of the present invention as cutting oil, the above-mentioned diluent can be used while provided for metal to be cut and cutting tools.

Water-based metal working oil of the present invention is superior in lubricity to steel and iron as well as lubricity to soft metal such as aluminum and aluminum alloy. That is to say, water-based metal working oil of the present invention is preferable for working aluminum, aluminum alloy, iron and/or steel.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is specifically described hereinafter by referring to examples, and is not limited thereto. Hereinafter, 'part' signifies 'part by weight'.

(1) Conditions of Mw measurement

measuring apparatus: LC8120 manufactured by Tosoh Corporation

eluant: THF

flow rate: 0.6 (ml/minute)

column: TSKgel Super H4000, H3000, H2000

primary standard: polyethylene glycol

(2) Measuring method of cloud point

The temperature at which a 2-weight % aqueous solution of (E) is heated and then clouding is confirmed by

visual observation was measured. The aqueous solution is transparent at a temperature of the cloud point or higher, and it is understood that a higher cloud point allows a more favorable water dilution stability.

5 (3) Calculating method of HLB

HLB was calculated by a method of calculation described on page 197 of 'New Introduction to Surface Active Agents' (1996, published by Sanyo Chemical Industries, Ltd.).

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(Examples 1 to 4, 7 and Comparative Example 1)

Aliphatic alcohol, THF and $\text{BF}_3 \cdot \text{THF}$ of the number of parts [parentheses signify molar ratio] described in Table 1 or Table 2 were charged into a glass-coated and stainless autoclave provided with a heating/cooling device, a stirring apparatus, a pressure-resistant dropping funnel, a nitrogen substitution tube and a thermometer, and EO of the number of parts [parentheses signify molar ratio] described in Table 1 and Table 2 was dropped thereinto through the pressure-resistant dropping funnel over 10 hours while maintained at a temperature of 35 to 50°C. Thereafter, the solution was aged at a temperature of 50°C for 5 hours and thereafter cooled. 48-weight % NaOH aqueous solution of the number of parts described in Table 1 and Table 2 was further added thereto so as to neutralize a catalyst and thereafter remove a low-volatile component thereof under a reduced pressure of 30 mmHg or less at a temperature of 120°C by distillation. Thereafter, the catalyst residue was adsorbed by using an adsorption treatment agent ("KYOWARD600 and KYOWARD1000, manufactured by Kyowa Chemical Industry Co., Ltd.") to thereafter filter and dehydrate under a reduced pressure (130°C, 30 mmHg or less and 1 hour, hereinafter in the same manner), and then obtain polyether (E1) to (E4), (E7) and comparative polyether (E'1), which were regarded as lubricants of

Examples 1 to 4, 7 and Comparative Example 1.

(Examples 5, 6 and 8)

Polyether by a random AO addition reaction was
5 manufactured and refined in the same manner as Example 1
except for changing the charged quantity of THF and EO to
the quantity described in Table 1 or Table 2. Then, the
polyether and potassium hydroxide were charged into the
10 same autoclave as Example 1 by the quantity described in
Table 1 and dehydrated under a reduced pressure, and
thereafter EO of the number of parts [parentheses signify
molar ratio] described in Table 1 was dropped thereinto
through the pressure-resistant dropping funnel over 10
hours at a temperature of 130°C. Thereafter, the solution
15 was further aged at a temperature of 130°C for 5 hours and
cooled, and then refined in the same manner as Example 1 to
obtain polyether (E5), (E6) and (E8), which were regarded
as lubricants of Examples 5, 6 and 8.

20 (Example 9)

1,000 parts of PTMG (1.0 mol; "PTMG1000, manufactured
by Mitsubishi Chemical Corporation"; PTMG having Mw of
approximately 1,000) and 0.4 part of KOH were charged and
dehydrated under a reduced pressure, and thereafter 1,012
25 parts (23 mol) of EO was dropped thereinto through the
pressure-resistant dropping funnel over 10 hours at a
temperature of 150°C. Thereafter, the solution was aged
over 10 hours until the pressure reached equilibrium at a
temperature of 150°C and cooled, and then refined in the
30 same manner as Example 1 to obtain 1,950 parts of a 23 mol-
EO block adduct of PTMG1000 (E9), which was regarded as a
lubricant of Example 9.

(Comparative Example 2)

35 76 parts (1 mol) of propylene glycol and 4.0 parts of

KOH were charged into the same autoclave as Example 1 and dehydrated under a reduced pressure, and thereafter 1,682 parts (29 mol) of PO was dropped thereinto through the pressure-resistant dropping funnel over 10 hours at a temperature of 105°C. Thereafter, the solution was aged over 8 hours until the pressure reached equilibrium at a temperature of 130°C, and thereafter 1,188 parts (27 mol) of EO was dropped thereinto through the pressure-resistant dropping funnel over 8 hours at a temperature of 130°C. Thereafter, the solution was aged over 5 hours until the pressure reached equilibrium at the same temperature and cooled, and then refined in the same manner as Example 1 to obtain 2,800 parts of a 29 mol-PO and 27 mol-EO block adduct of propylene glycol (E'2), which was regarded as a lubricant of Comparative Example 2.

The yield, Mw, HLB and cloud point of (E1) to (E9) and (E'1) and (E'2) are shown in Table 1 and Table 2.

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Table 1

		Example					
		1	2	3	4	5	6
5	Product Name of Polyether	E 1	E 2	E 3	E 4	E 5	E 6
10	Random or Block AO Addition Reaction	1,4-Butanediol	90 (1)	90 (1)	90 (1)	90 (1)	90 (1)
		Glycerin					
		Propylene Glycol					
15		THF	216 (3)	1008 (14)	792 (11)	504 (7)	1512 (21)
		EO	176 (4)	880 (20)	1100 (25)	1408 (32)	440 (10)
20		PO					
		BF ₃ · THF	3.2	12.8	12.8	12.8	17.0
		48% NaOH Aqueous Solution	1.9	7.4	7.4	7.4	9.8
25	Second-step AO Addition Reaction	EO				220 (5)	220 (5)
		KOH				1.2	1.4
30	Yield (part)	460	1880	1883	1902	2150	2628
	Mw	500	2150	2180	2200	2490	3040
	HLB	11.7	9.9	11.7	14.3	7.4	6.5
35	Cloud point (°C)	21	21	34	46	13	10

Table 2

		Example			Comparative Example	
		7	8	9	1	2
5	Product Name of Polyether	E 7	E 8	E 9	E' 1	E' 2
10	Random or Block AO Addition Reaction	1,4-Butanediol	90 (1)		90 (1.0)	
		Glycerin	92 (1)			
		Propylene Glycol				76 (1)
15		THF	1152 (16)	1512 (21)	1,000 parts of PTMG-1000 (1)	1512 (21)
		EO	1760 (40)	1760 (40)		352 (8)
		PO				1188 (27)
20		BF ₃ · THF	19.1	12.8		1682 (29)
		48% NaOH Aqueous Solution	11.0	7.4		12.8
25	Second-step AO Addition Reaction	EO		5720 (130)	1012 (23)	
		KOH		5.6	0.4	
30	Yield (part)		2850	8630	1950	1860
	Mw		3300	9990	2100	2150
	HLB		12.4	15.6	10.7	5.9
35	Cloud point(°C)		39	>70	25	Absent
						58

(Examples 10 to 21 and Comparative Examples 3 to 6)

Components except water were compounded on the basis of compounding proportions (part) described in the following Table 3 and thereafter sufficiently mixed at room temperature to obtain a lubricant composition.

Triethanolamine, 4 mol of ethylenediamine (PO) and 5 mol of diethylenetriamine (PO) were used as a neutralizer of carboxylic acid, and the excessive equivalent was a rust preventive (J).

Water of the number of parts described in Table 3 was further added to these lubricant compositions and sufficiently mixed at room temperature to obtain water-based metal working oil of Examples 10 to 21 and Comparative Examples 3 to 6. The appearances of these water-based metal working oils are shown in Table 3.

The criterion for evaluation of the appearances is as follows:

Excellent: uniformly transparent

Poor: separated into two layers

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Table 3

		Example												Comparative Example				
		10	11	12	13	14	15	16	17	18	19	20	21	3	4	5	6	
5	Polyether (E)	E 1	40															
		E 2		40								40	40	40				
		E 3			40													
10		E 4				40												
		E 5					40											
		E 6						40										
		E 7							40									
15		E 8								40								
		E 9									40							
		E' 1													40	40		
		E' 2															40	40
20	(F) + (J)	Caprylic Acid	5	5	5	5	5	5	5	5	5		5	5	5		5	30
		Sebacic Acid										4				4		
		Triethanolamine	5	5	5	5	5	5	5	5	5	5			5	5	5	5
25		4 mol of Ethylenediamine (PO)											10					
		5 mol of Diethylenetriamine (PO)												20				
30	Water		50	50	50	50	50	50	50	50	50	51	45	35	50	50	50	25
	Appearance		Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Poor	Excel-lent	Excel-lent	Excel-lent

The results of evaluating water dilution stability and lubricity of these water-based metal working oils by the following measuring method are shown in Table 4.

5 <Preparation of test liquid>

The water-based metal working oils of Examples and Comparative Examples were further diluted with water by twenty times to prepare test liquid.

10 <Water dilution stability>

The test liquid was charged into a 100-mL measuring cylinder with a glass stopper to determine the appearances after one day at a temperature of 25°C through visual observation by the following standard.

- 15 Excellent: uniformly transparent
- Fair: slightly cloudy
- Poor: separated into two layers

<Lubricity>

- 20 The lubricity was evaluated by measuring the friction coefficient and oil film shortage of the test liquid in a point contact (a load of 100 g) with a steel ball, plane steel plate and aluminum plate with the use of a ball-on-disk type frictional wear tester ("friction player FPR-2000, 25 manufactured by Rhesca Co., Ltd.").

Testing conditions are as follows:

- number of revolutions: 20 rpm
- radius of gyration: 15 mm
- temperature: 30°C
- 30 time: 5 minutes
- friction coefficient (μ): average value over 5 minutes

The evaluation of the oil film shortage was determined by the variation of μ observed within the measuring time, which evaluation is as follows:

- 35 Excellent: the variation of $\mu < 0.025$

Fair: $0.025 \leq \text{the variation of } \mu \leq 0.040$

Poor: the variation of $\mu > 0.040$

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Table 4

5	Used Water-based Metal Working Oils		Appearance of Diluent with Water	Lubricity to Steel Plate		Lubricity to Aluminum Plate	
				Oil Film Shortage	Friction Coefficient	Oil Film Shortage	Friction Coefficient
10 15 20	Example	1 0	Excellent	Excellent	0.105	Excellent	0.090
		1 1	Excellent	Excellent	0.093	Excellent	0.073
		1 2	Excellent	Excellent	0.091	Excellent	0.074
		1 3	Excellent	Excellent	0.097	Excellent	0.080
		1 4	Excellent	Excellent	0.100	Excellent	0.085
		1 5	Excellent	Excellent	0.102	Excellent	0.086
		1 6	Excellent	Excellent	0.095	Excellent	0.075
		1 7	Excellent	Excellent	0.120	Excellent	0.100
		1 8	Excellent	Excellent	0.105	Excellent	0.095
		1 9	Excellent	Excellent	0.097	Excellent	0.065
		2 0	Excellent	Excellent	0.091	Excellent	0.063
		2 1	Excellent	Excellent	0.090	Excellent	0.065
25 30	Comparative Example	3	Poor	Excellent	0.130	Excellent	0.110
		4	Excellent	Poor	0.170	Poor	0.136
		5	Excellent	Poor	0.139	Poor	0.175
		6	Excellent	Poor	0.210	Poor	0.160

INDUSTRIAL APPLICABILITY

A lubricant for water-based metal working oil of the present invention is extremely effective as a lubricant for

water-based metal working oils such as cutting oil, rolling oil, drawing oil, pressing oil, forging oil, abrasive working oil for aluminum disk, abrasive oil for silicon wafer and coolant for cutting silicon wafer.

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